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<b>(21) International Application Number:</b> PCT/FI95/00085 <b>(22) International Filing Date:</b> 20 February 1995 (20.02.95) <b>(30) Priority Data:</b> 941783 18 April 1994 (18.04.94) FI <b>(71) Applicant (for all designated States except US):</b> NESTE OY [FI/FI]; Keilaniemi, FIN-02150 Espoo (FI). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> KARHU, Esa [FI/FI]; Lyhdetie 11, FIN-06150 Porvoo (FI). KÄRNÄ, Toivo [FI/FI]; Kuskintie 3, FIN-06400 Porvoo (FI). LAAKSO, Jukka [FI/FI]; Ruusulankatu 16 B 24, FIN-00250 Helsinki (FI). SUOMINEN, Matti [FI/FI]; Putkistontie, FIN-37120 Nokia (FI). JUSSILA, Matti [FI/FI]; Rypsikuja 1 D, FIN-06400 Porvoo (FI). KIRMANEN, Pauli [FI/FI]; Kantokuja 6, FIN-06450 Porvoo (FI). <b>(74) Agent:</b> NESTE OY; Patent Services, P.O. Box 310, FIN-06101 Porvoo (FI).		<b>(81) Designated States:</b> AU, CA, CH, CN, DE, DK, ES, GB, JP, KR, LU, NL, NO, PT, RU, SE, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i> <i>In English translation (filed in Finnish).</i>
<b>(54) Title:</b> ELECTRICALLY CONDUCTING MATERIAL AND A METHOD TO PREPARE IT  <b>(57) Abstract</b>  <p>The invention relates to electrically conductive plastics blends which contain a polyaniline complex doped with a protonic acid, the blends having been prepared by dry-mixing together an electrically conductive polyaniline complex and a matrix plastic. The dry blend according to the invention is a melt-processible, homogeneous material the electrical conductivity properties of which are very good even at low conductive polymer contents. The invention also relates to a method for the preparation of such a dry blend. It is possible to add to the dry blend more matrix plastic and any necessary plastics additives and to process the blend with conventional plastics processing methods into the desired end products. Preferred end products include the shielding casings, packaging cases and transport cases for sensitive electronic devices, as well as various floor covering materials.</p>		

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ELECTRICALLY CONDUCTING MATERIAL AND A METHOD  
TO PREPARE IT

- 5 The invention relates to an electrically conductive plastics blend which contains a polyaniline complex doped with a protonic acid and which is prepared by dry mixing an electrically conductive polyaniline complex and a matrix plastic. The invention also relates to a method for preparing such an electrically conductive dry blend. The blend thus obtained may be processed further into desired end products by using conventional plastics  
10 processing methods.

Electrically conductive plastics blends in which the conductive component is an intrinsically conductive polymer can be prepared according to the state of the art by mixing in molten state an electrically conductive polymer and a matrix plastic. The electrically  
15 conductive components used may also be various other conductive particles, for example carbon black, metals, and various powders and fibers, such as carbon fibers.

Typical electrically conductive plastics products include various films, coatings such as plastic floor coverings, sheets, pipes, various formed pieces, etc. The most common areas  
20 of use include various targets requiring EMI and ESD shielding, for example in the packaging industry, the electronics industry, the coating of spaces requiring shielding, etc.

Intrinsically conductive polymers are produced by adding to polymers suitable oxidizing or reducing agents, i.e. dopants. These serve in the polymer as electron acceptors or  
25 electron donors, whereby electron holes or excess electrons are formed in the polymer, enabling electric current to travel along the conjugated chain. Examples of intrinsically conductive polymers known in the art include polyacetylene, poly-p-phenylene, polypyrrole, polythiophene with its derivatives, and polyaniline with its derivatives.

- 30 Polyaniline with its derivatives has proved to be a technically and commercially promising electrically conductive polymer. Polyaniline may be present in a number of forms, which include leucoemeraldine, protoemeraldine, emeraldine, nigraline and tolupprotoemeraldine forms.

- Polyaniline can be rendered electrically conductive by being doped with a protonic acid, such as protonic mineral acids or organic acids. Examples of doping acids used include HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, HClO<sub>4</sub>, HBF<sub>4</sub>, HPF<sub>6</sub>, HF, phosphoric acids, sulfonic acids, picric acid, n-nitrobenzoic acid, dichloroacetic acid, and polymeric acids. Preferably the doping
- 5 is carried out using sulfonic acid or its derivatives, and dodecylbenzenesulfonic acid (DBSA) has proved to be the most preferable doping acid. However, such a doped polyaniline is as such a staining or corrosive liquid or viscous material which is difficult to handle.
- 10 EP patent publication 545 729 discloses a method for bringing a polyaniline doped with a protonic acid to an easy-to-handle, melt-processible form by heat treating it with sulfonic acid or its derivative at a temperature of approx. 40 °C - 250 °C.
- EP patent publication 582919 further discloses a method by which it is possible to produce
- 15 an electrically conductive, melt-processible polyaniline complex which has a substantially neutral pH and is easy to handle. By decreasing the acidity, of course, the problems of corrosion of the polymer production and processing apparatus is reduced. This is achieved by adding a metal compound, most preferably zinc oxide, to the polyaniline protonated with a protonic acid and the sulfonic acid or its derivative, most preferably dodecylben-
- 20 zenesulfonic acid, plasticizing the polyaniline. By plasticization is meant the rendering of the polymer such that it can be further processed to the desired form for application.
- An electrically conductive, melt-processible polyaniline complex, having a substantially neutral pH, prepared by the methods described above, can be mixed, as is also stated in
- 25 the above-mentioned publications, by conventional melt-mixing methods with any matrix plastics generally used for this purpose. The most common matrix plastics include homo- or copolymers based on, for example, olefins, styrene, vinyl polymers or acrylic polymers, or their mixtures or thermoplastic condensation polymers. Some of the most commonly used matrix polymers include polyethylene, polypropylene, styrene butadiene,
- 30 polystyrene, polyvinyl chloride, polyamide, and polyester.

The proportion mentioned for the conductive polymer complex in such plastics blends prepared by melt-mixing methods is 1-50 % by weight, preferably 1-25 % by weight, and

most preferably 5-15 % by weight. In order to achieve sufficiently high conductivity properties, such plastics blends should, however, in general contain the conductive polymer complex at least in an amount of 5 % by weight; most often the amount of the complex is at a level of approx. 10 % by weight.

5

In addition to the conductive component and the matrix plastic the electrically conductive plastics blends contain, depending on the matrix polymer and the targeted use, for example softeners, stabilizers, pigments, mold lubricants, modifiers, and fillers. The most commonly used softeners, for example in PVC products, are derivatives of phthalic acids, such as phthalates, of which the most commonly used is dioctyl phthalate (DOP). When necessary, it is also possible to use derivatives of other acids, such as epoxy (e.g. epoxated soybean oil), adipic and phosphoric acids. The stabilizers are most commonly metal soaps, inorganic acids (such as barium and lead salts), organostannium compounds, and epoxy compounds. Both organic and inorganic pigments and dyes can be used as coloring agents. The mold lubricants may be, for example, long-chain alcohols or various waxes.

Plastics blends containing a conductive polyaniline complex as described above are thus prepared, as stated above, by a melt mixing method. In plastics blends, however, the processibility of the electrically conductive, protonic acid doped and plasticized polyaniline complex present in the plastics blends is limited with respect to the common plastics processing temperatures and methods. Problems may appear in both the structural stability and the stability of the electrical conductivity of the polyaniline complex. Since in the polymer melt-mixing step the temperature must be raised above the thermal resistance limit of the doped polyaniline complex, destruction of the polymer blend will follow within a very short time. For example, the typical processing temperature of PVC is within the range 165 °C - 180 °C. Since in the polymer melt-mixing step the temperature must be raised to this range, destruction of the polymer blend will follow already within a few minutes. Consequently, the time of the further processing of the plastics blend has to be shortened significantly, and this, of course, will cause problems in the proper completion of the further processing step. For example, the total processing time of PVC already at 150 °C is only a few minutes. In other words, both the melt mixing, i.e. compounding, of the polymer blend and its further processing step must be performed

within this time, a factor which, of course, causes problems in the manufacture of products.

Furthermore, with very low contents of conductive polymer, below 5 % by weight, sufficient conductivity properties are usually not achieved in plastics blends prepared by melt-mixing methods. However, maximally low contents of conductive polymer would often be highly desirable for reasons of both cost and product properties of the plastics blend.

Furthermore, it is known that, if a polymer material has to be melted and cooled several times, its properties will deteriorate significantly, as the melt index will change in consequence to the successive melting/cooling treatments. This is precisely what occurs in a case in which a plastics blend is prepared by melt mixing and this blend is further processed by various melt-mixing methods in a subsequent step.

15

When melt-mixing methods are used, problems may arise also with respect to certain plastics blend additives, such as pigments, stabilizers, plasticizers, and lubricants.

The preparation of a plastics blend simply by mixing as such an electrically conductive polyaniline complex and a matrix plastic is not possible in terms of a satisfactory end result. A product so prepared is a material which produces dust, is difficult to handle, and is non-homogenous. When such a material is transported and stored, separation of the various components, i.e. the conductive particles and the matrix polymer particles, will occur in it, and as a result the material will have an unevenly distributed conductivity, which in turn will cause the processed end product to be uneven in quality.

It is true that electrically conductive plastics blends can also be prepared by using dry-mixing techniques, known per se. In this case the conductive component used is carbon black, metals, various powders, and fibers, such as carbon fibers. However, the use of such components causes, for example, problems associated with the outer appearance of the product (e.g. color problems), mechanical and technical problems, and problems associated with the control of the conductivity level. Intrinsically conductive polymers have not previously been used in such blends prepared by dry-mixing techniques.

By dry mixing is meant the mixing of the components with each other in high-speed mixers, which include friction mixers, which typically have a cooling mantle by means of which excessive elevation of the temperature during mixing can be prevented.

- 5 Examples of the use of carbon black in the form of a softener dispersion in a PVC matrix include US patent publications 4 976 890 and 5 066 422. In the methods described in these publications, a preliminary blend (softener, carbon black and stabilizers) is combined with a porous PVC resin. The temperature in the mixing step must not rise above 70 °C.

10

The composition disclosed in EP patent publication 539 936 comprises a thermoplastic polymer and, as the conductive material, a short fiber derived from carbon or germanium. These can be combined by dry mixing or by compounding the mixture in, for example, an extruder.

15

US patent publication 5 217 649 discloses a plastics blend in which the conductive polymer, such as polyaniline, is dispersed in a matrix plastic which contains a sulfonamide softener. What is in question is thus not a dry blend of an electrically conductive polymer and a matrix plastic.

20

US patent publication 5 254 633 discloses a process for the preparation of a plastics blend, in which process matrix polymer particles and conductive polymer particles are contacted with each other by means of a medium which serves as a solvent. This medium must subsequently be removed from the blend, for example by evaporation, before the  
25 further processing of the blend.

- EP patent publication 497 514 discloses a blend of PVC, doped polyaniline, a softener, and additives, the blend being formed by dispersing polyaniline into PVC in a 2-roll mill. According to the publication, highly polar, ester-free softeners, such as sulfonamides,  
30 must be used as the softener, since, according to the publication, polyaniline reacts with conventional softeners, such as esters, used with PVC, thus causing a weakening of the conductivity.

EP patent publication 500 054 further discloses a dry blend of two resins and a process for its preparation, the purpose being to produce a carrier for a two-component developing agent for the developing of electrostatic latent pictures. According to the process of the publication, for example seed particles formed of ferromagnetic metals and alloys, as well  
5 as a fluorine-containing resin and a resin having a lower melting point than the first-mentioned resin, are dry mixed together, and the mixture is heated while stirring so that the coating resin, having a lower melting point, will soften and melt and coat the seed particles with a continuous coating layer. This is followed by a cooling to prevent agglomeration of the carrier particles. This publication, however, does not describe the  
10 use of a conductive polymer in the blend.

A further example of dry mixing is US patent publication 4 889 673, which describes a dry-mixing process for a suspension PVC to be used for extrusion molding, a softener, stabilizer and pigments by using a mixer having a high shear force. The temperature  
15 during mixing is maintained below 165 °C, preferably the mixing temperature is 80 °C - 110 °C, i.e. the temperature must be well below the melting temperature of PVC, which is 170 °C. The blend thus obtained is kneaded and pelleted by extrusion. However, the process according to this publication includes neither the use of conductive particles in the preparation of the blend nor the mixing of different polymers with each other.

20

The publications discussed above disclose solutions to the problem of producing an electrically conductive plastic material and dry mixing methods of different components. Obtaining electrical conductivity by the use of carbon fiber or a similar conductive filler is often not a desirable solution; the disadvantages include color problems and also the  
25 weakening of the mechanical and certain chemical properties as the filler content increases. The control of the electrical conductivity when using conductive filler particles may also be difficult, especially at low conductivity levels. According to above-mentioned EP patent publication 497 514, a satisfactory end result for a conductive PVC material is also not obtained by using conventional softeners of PVC, such as phthalates.  
30 Furthermore, it is to be noted that, according to this publication, the polyaniline is dispersed in the matrix, and no results regarding this dispersion remaining a homogenous material are disclosed. Furthermore, it is important to note that no pH values of the polyaniline-matrix dispersion are presented, and it can be assumed that they are acid



compositions. The polyaniline used in these blends is not a doped and plasticized, substantially neutral polyaniline.

Thus, none of the processes described produces, by a method simple in terms of process technology, an electrically conductive, preferably substantially neutral, homogenous and stable plastics blend having a controllable stability and retaining its homogeneity, which plastics blend can be easily processed further by any commonly used plastics processing methods and is prepared by dry mixing together a matrix polymer and an electrically conductive, doped and plasticized, substantially neutral polyaniline.

10

An object of the present invention is thus to provide an electrically well conductive plastics blend prepared by dry-mixing techniques, in which blend the conductive component is a polyaniline complex doped with a protonic acid and containing a plasticizing agent, and the matrix polymer consists of one or several commonly used matrix plastics, and which blend is suitable for being further processed by conventional plastics processing methods.

20

Another object of the invention is a plastics blend in which better electrical conductivities are achieved with a lower content of conductive polymer and in which the conductivity withstands the processing of the blend into the desired end products.

25

It is a further object to obtain an electrically conductive plastics blend having a high attenuation capacity and a good microwave absorption correlating with the electrical conductivity.

30

It is also an object of the invention to achieve a plastics blend, prepared by dry-mixing techniques, the acidity of which may range from acid to nearly neutral; preferably, however, its acidity is substantially within the neutral pH range, i.e. within a pH range of approx. 3.5 - 7.

It is a further object to prepare a dry blend of plastics which contains a protonic acid doped and plasticized polyaniline complex, the polymer components of the blend being capable of being mixed together without worsening the polymer melt index.

It is also an object of the invention to prepare an electrically conductive plastics dry blend the mechanical properties of which are comparable with corresponding electrically conductive plastics blends prepared by melt-mixing methods.

- 5 It is still another object of the invention to achieve an electrically conductive plastics dry blend, which remains homogenous, i.e. in which separation and division of the different particles will not take place, for example during transport and storage.

Furthermore, it has been desired to produce a dust-free, electrically conductive plastics  
10 dry blend which is easy to handle.

It is still another object of the invention to obtain an electrically conductive dry blend in the form of a master batch, to which the onward user of the blend may add a matrix polymer, fillers and any desired additives, such as softeners, stabilizers, pigments,  
15 foaming agents, etc.

It has now been observed, surprisingly, that the mixing together of a matrix polymer and a conductive polymer complex may, instead of compounding in molten state, be conducted by dry mixing the components with each other in a dry mixer the temperature of which  
20 can be adjusted and by selecting a suitable plasticizer for the polyaniline. The mixing must be carried out at so low a temperature that thermal decomposition of the polymer will not occur, but at such a temperature that a dry blend according to the invention, having the properties stated above, will be formed. This can be done by selecting a suitable compound which plasticizes the doped polyaniline. An electrically conductive dry blend which  
25 contains a protonic acid doped polyaniline and a matrix polymer/matrix polymers is thus characterized in what is stated in the characterizing clause of Claim 1.

The preparation of an electrically conductive dry blend according to the invention is thus based on the fact that, when the plasticizer melts on the complex particle during mixing,  
30 the temperature being below 125 °C, preferably below 120 °C, the complex particle easily adheres to the surface of a matrix polymer particle, and thereby a dust-free dry plastics blend which is easy to handle is produced. Furthermore, separation of matrix polymer particles and complex particles, due to a weight and size difference, is prevented.

It can be said that the molten plasticizer serves as if as a "glue" between the complex particles and the matrix polymer particles in the blend. It is important that the plasticizer is selected so that its melting temperature is so low that thermal decomposition of the polymer will not occur.

5

In such a dry blend according to the invention, the compound used as the plasticizer must thus be a compound which is capable of plasticizing the conductive polyaniline at a temperature lower than the plasticization temperature of the matrix polymer. There must also be a sufficient difference between the plasticization temperatures of the polymer  
10 complex and the matrix polymer for a dry blend according to the invention to be formed. If the plasticization temperatures of the polyaniline complex and the matrix polymer are very close to each other, i.e. the differences are below an order of 10 °C, the consequence is that the conductive polymer complex and the matrix polymer will blend physico-chemically with each other, the result not being a dry blend.

15

A dry blend according to the invention is thus prepared at a temperature at which thermal decomposition of the conductive polyaniline does not occur but at which its plasticization can take place. These requirements are fulfilled when the mixing takes place at a temperature below 125 °C, preferably below 120 °C, but above 80 °C. The lower limit for the  
20 temperature is, of course, determined by the melting range of the plasticizer. Suitable plasticizers, which melt and plasticize the polyaniline in a complex at a temperature below 120 °C and by means of which the desired properties of a plastics blend, stated earlier in this specification, are accomplished include sulfonic acid derivatives, most preferably dodecylbenzenesulfonic acid, together with a zinc compound, preferably zinc oxide.

25

In other words, in a dry blend according to the invention the melting properties of the plasticizer are exploited, which further affect the plasticization of the polymer. The plasticization can also be described by the viscosity difference of the polymers so that the plasticized polymer complex has a lower viscosity than has the matrix polymer.

30

The mixing of the conductive polymer complex and the matrix polymer is preferably carried out in high-speed mixers, one such mixer being the so-called friction mixer, in which the temperature rises during mixing but excessive rising of its temperature can be

prevented by means of a cooling mantle in the mixer.

With respect to their particle size, the matrix polymer particles and the polyaniline complex particles may be:

5 a) of equal size

b) the matrix polymer particles larger than the complex particles or

c) the matrix polymer particles smaller than the complex particles.

In case a) the particles are evenly mixed in the dry blend. In case b) the complex particles coat the matrix polymer particles, and in case c) the matrix polymer particles for their  
10 part coat the complex particles.

In all cases the end result is a homogenous, evenly electrically conductive dry blend material. Differences between the particle sizes of the components affect, among other things, the flow and rheological properties of the dry blend. Regulation of the size  
15 differences between the particles, for example by a conventional screening method, thus offers a simple and ingenious method of affecting the said factors affecting the processing properties, without weakening the homogeneity or electrical conductivity properties of the material.

20 An improvement of the homogeneity of the blend is thus a significant advantage in the process according to the invention. An advantageous conductivity network structure is already formed in a dry blend prepared according to the invention, and this structure will not substantially change in conventional processing screws designed for the melting and homogenization of plastics. This blend homogeneity, with respect to the structure and thus  
25 also the conductivity, is also retained during, for example, transport and storage, since separation of the particles from each other will not occur.

Since the temperature will not rise above 125 °C, preferably not above 120 °C, no thermal decomposition of the polymer will occur during the preparation of the blend, and  
30 the total processing time thereby saved can be carried over to the processing of the end product to be prepared; this, of course, facilitates and expands the possibilities for processing a plastics blend containing a conductive polyaniline complex.

The electrically conductive dry blend material is made especially advantageous from the viewpoint of the onward user by the fact that any necessary additives and also a matrix polymer can be added to it, depending on the end products. The dry blend can be regarded as if it were a "concentrate" with which it is possible to mix, i.e. which is capable of binding to itself, other necessary ingredients. The performer of the processing can thus add to this dry blend material, depending on the intended use, a necessary amount of a matrix polymer, such as polyolefins or PVC for example in the form of plastic granulates or powder, softeners, stabilizers, pigments, and other desired additives. The additives may be added to the blend either during its preparation or to the completed blend. Such a dry blend material according to the present invention is, from the viewpoint of not only the supplier of the blend but also the onward user, very practical in terms of the production of an electrically conductive plastics material, its further delivery, and its use for various processing applications.

The polyaniline doped with a protonic acid, used in a plastics blend according to the invention, prepared by dry mixing techniques is plasticized and heat treated at a temperature of 40 °C - 300 °C, preferably 60 °C - 250 °C. The doping protonic acid may be, as stated, a mineral acid or an organic acid. Dodecylbenzenesulfonic acid is a commonly used doping acid. The plasticizer used must thus melt at a temperature below 120 °C. Such a compound is most preferably a compound formed by DBSA and zinc oxide ZnO. A Zn-DBSA compound melts at approx. 110 °C, and thus it is highly suited for use in a dry blend according to the invention, not only because of these suitable melting properties but also because of its good plasticizing properties noted previously. When softening and melting, a Zn-DBSA compound will cause the conductive polyaniline complex particles to adhere during dry mixing to the surfaces of matrix polymer particles, and thus the result will be a dust-free, homogenous, highly electrically conductive plastics blend material which retains its homogeneity well.

The plasticized, electrically conductive polyaniline complex used in a dry blend material according to the present invention may have a pH value ranging from acid to nearly neutral. It is, however, usually more advantageous considering the various processing and other apparatus coming into contact with the electrically conductive polyaniline complex that the pH of the complex is substantially within the neutral range. By this is meant in

this context a pH range of approx. 3.5 - 7. Preferably the pH value is within the range 4 - 6.5.

A plastics dry blend according to the present invention, containing an electrically  
5 conductive polyaniline complex, is prepared by using the dry-blending techniques known  
per se. An electrically conductive polyaniline complex which contains the plasticizer is  
first ground using a shear-action mill to a finely-divided powder. The screen used may be,  
for example, a screen of 0.5 - 1.5 mm. The molar ratio of the plasticizer to the doped  
polyaniline may vary within a range of approx. 1 : 0.1 - 1 : 3, preferably within the range  
10 1 : 0.25 - 1 : 1, and most preferably within the range 1 : 0.5 - 1 : 0.7. If the plasticizer  
used is a Zn-DBSA compound and the doping acid is DBSA, the polyaniline complex  
typically contains plasticizer approx. 10 - 50 % by weight and doped polyaniline approx.  
90 - 50 % by weight, preferably plasticizer approx. 20 - 40 % by weight and doped  
polyaniline approx. 80 - 60 % by weight. The amount of plasticizer affects not only the  
15 result of the plasticization but also the acidity of the polyaniline complex.

After the grinding, the plasticized polyaniline complex is mixed with the matrix plastic in  
a high-speed mixer, such as a friction mixer, at a temperature below 125 °C, preferably  
below 120 °C. When such a mixer is used, the mixing time is approx. 10 - 30 min.  
20 Thereafter the blend is cooled while mixing is continued. The proportion of matrix  
polymer may vary within a wide range, i.e. approx. 99 - 50 % by weight, depending on  
the desired conductivity level and on the additives added at this stage. The result obtained  
is a homogenous, electrically well conductive, easy-to-handle dust-free plastics dry blend  
which retains its conductivity and homogeneity, the acidity of which can be adjusted, and  
25 which can be further processed into the desired end products.

More matrix plastic or matrix plastics and desired additives can be further mixed with the  
conductive dry blend obtained from the step described above. The matrix plastic may be  
in pulverous or granulate form, the pulverous form being, however, generally preferable.  
30 The essential point is that a dry blend material is obtained which adapts flexibly to the  
needs of the onward user.

The conductivity level attained with a smaller conductive polymer content in the plastics

dry blend material according to the invention is significantly better than that in a product prepared by a conventional melt-mixing method. The achieved conductivity level is preferably at a level  $> 10^{-9}$  S/cm, preferably at a level  $> 10^{-6}$  S/cm, and most preferably at a level  $> 10^{-3}$  S/cm. For example, at a conductive polyaniline complex content as low  
5 as 3 % by weight, an electrical conductivity (ESD) is achieved, which can be regarded as a very good achievement. In injection molded pieces made from a dry blend according to the invention, conductivities are achieved which better than prior art make EMI and microwave applications possible. It can also be pointed out that with a dry blend having a 5 % by weight polyaniline complex content, conductivity values of  $10^{-4}$  -  $10^{-5}$  S/cm are  
10 achieved in injection molded pieces, but if the polyaniline complex is mixed with the matrix plastic by the melt-mixing method, the conductivity of specimens injection molded from such a blend is clearly weaker.

In addition, pieces made from a dry blend according to the invention have a good  
15 attenuation capacity, which property can be exploited, for example, in the manufacture of shielding casings of sensitive electronic devices, such as computers. The antistatic properties of products made from the dry blend can, for their part, be exploited, for example, in transportation and packaging cases for electronic equipment, floor covering applications, etc.

20

In floor covering applications (PVC floor coverings), the suitable electrical conductivity, defined by standards, is at a level of  $10^{-6}$  -  $10^{-8}$   $\Omega$ . A typical floor covering material composition may in the main contain, for example, in total 10 % a blend which contains 30 % a Zn-DBSA compound and 70 % doped polyaniline, and 90 % a mixture which contains  
25 approx. 50 % PVC and 50 % filler.

Furthermore, it can be stated that pieces injection molded from a plastics dry blend according to the invention have moderate and highly comparable mechanical properties as compared with pieces made from a melt-mixed blend.

30

The invention is described in greater detail in the following figures and examples. The phr unit (= parts per hundred parts of resin) appearing in Examples 4 - 8 is a quantity unit commonly used especially in PVC applications.

Figure 1. A microscopic picture of PVC particles with polyaniline-DBSA complex particles adhering to their surfaces.

Figure 2. An enlarged detail of a PVC particle with polyaniline-DBSA complex particles  
5 adhering to its surface.

Figure 3. A microscopic picture of a polyaniline-DBSA complex particle with PVC particles adhering to its surface.

10 Figure 4. A microscopic picture of PVC particles with polyaniline-DBSA complex particles adhering to their surfaces.

Figure 5. Shielding efficiency of an injection molded piece made from a dry blend according to the invention, as a function of the frequency of the incident radiation.

15

Figure 5 depicts the shielding efficiency, i.e. the attenuation capacity (in decibels dB), of a piece injection molded from a dry blend prepared according to Example 1, as a function of the frequency of the incident radiation. It can be seen from the figure that the shielding efficiency drops by approx. 20 dB when the frequency increases by one order, from the  
20 5th exponential to the 6th exponential, but remains unchanged thereafter up to the 8th exponential.

#### Example 1

Preparation of an electrically conductive dry blend.

25 An electrically conductive, solidified polyaniline complex was prepared in which the proportion of polyaniline doped with dodecylbenzenesulfonic acid (DBSA) was 60 % by weight and the proportion of the Zn-DBSA compound used as the plasticizer was 40 % by weight.

30 This complex was mixed with the polypropylene powder (VB 6550B, manufacturer Neste Oy) used as the matrix polymer and with Ketjenflex 9S sulfonamide additive at the weight ratio 47.5 : 47.5 : 5 in a friction mixer (Henschel FM10L). The mixing time was 16 minutes and the temperature was at maximum 125 °C. The mixture was cooled for 15



minutes while mixing was continued. The size of the batch mixed was 1000 g.

### Example 2

A master batch dry blend prepared in accordance with Example 1 was further mixed by  
 5 dry-mixing the homopolymer with the polypropylene VB 6550B at different ratios. Round  
 pieces were formed from the blend in an injection mold KM210. Table 1 shows the  
 master batch contents, complex contents, and the contents of the added polypropylene in  
 the blends prepared.

10 Table 1. Component contents in the dry blend.

Sample	MB/wt-%	Complex/wt-%	PP/wt-%
1	100	47,5	-
2	5	2,38	95
3	7,5	3,56	92,5
4	10,5	4,99	89,5
5	15	7,13	85
6	20	9,15	80
7	30	14,3	70

20

Conductivities of the round pieces obtained from the injection mold were measured on the same day (a), on the next day (b), and 10 days (c) after the making of the piece. The results are shown in Table 2.

5 Table 2. Conductivities of injection molded pieces.

Sample	Conductivity / S/cm		
	a	b	c
2	$2,09 \cdot 10^{-12}$	$2,05 \cdot 10^{-12}$	$2,00 \cdot 10^{-13}$
3	$5,42 \cdot 10^{-7}$	$5,33 \cdot 10^{-5}$	$3,90 \cdot 10^{-4}$
4	$9,06 \cdot 10^{-7}$	$2,30 \cdot 10^{-5}$	$4,72 \cdot 10^{-4}$
5	$3,33 \cdot 10^{-2}$	$7,04 \cdot 10^{-4}$	$8,40 \cdot 10^{-3}$
6	$3,33 \cdot 10^{-2}$	$7,38 \cdot 10^{-5}$	$1,80 \cdot 10^{-3}$
7	$3,30 \cdot 10^{-2}$	$3,32 \cdot 10^{-2}$	$1,70 \cdot 10^{-2}$

**Example 3****Microwave absorption experiments.**

- a) Reference samples. Reference samples (5 samples) were prepared, in which the doped polyaniline complex was mixed directly with the matrix polymer VB 6550B by the melt-mixing method in an injection mold and was processed into test sheets. The absorption capacity of the sheets per wavelength, i.e. their attenuation coefficient  $\tan(\delta)$  at the frequency 11 GHz, was measured. The contents of the complex and the matrix polymer and the obtained attenuation coefficients are shown in Table 3. The reference samples are indicated by the code MaK 1-5.

10

- b) Method according to the invention. Five samples were prepared, in which the doped polyaniline complex, Kentjenflex 9, and the matrix polymer, VB 6550B, were first mixed into a master batch blend by the dry-mixing method according to the invention, and this blend was further dry mixed with additional matrix (VB 6550B). Sample sheets were molded from the blend, and their attenuation coefficients were measured as in a). The contents of complex, master batch and additional matrix, as well as the attenuation coefficients measured, are shown in Table 3. The specimens according to the invention are indicated by the code MaD 1 - 5.

Table 3. Attenuation coefficients of the reference samples and the samples according to the invention.

Sample	MB/wt- %	Compl./wt- %	PP/wt- %	tan( $\delta$ )
MaK1	-	5	95	0,12
MaK2	-	10	90	0,19
MaK3	-	20	80	0,23
MaK4	-	30	70	0,21
MaK5	-	40	60	0,28
MaD1	10,5	5	89,5	0,28
MaD2	21,05	10	78,95	0,44
MaD3	42,1	20	57,9	0,37
MaD4	63,15	30	36,85	0,56
MaD5	84,2	40	15,8	-

#### Example 4

A polyaniline-DBSA complex (10 phr) comminuted by means of a shear-action mill (1 mm screen) and Neste Oy's PVC resin S88Y (90 phr) were mixed in a friction mixer while raising the temperature to 110 °C in the course of approx. 15 minutes. Thereafter the blend was cooled while the mixing was continued. Microscopic pictures, Figures 1 and 2, were taken of the blend formed. The basic idea of the present invention, i.e. that the complex particles adhere to the surfaces of the PVC particles with the help of the molten Zn-DBSA compound used as the plasticizer, is clearly observable in these figures.

When coarser complex particles were selected for the preparing of the dry blend, polyaniline-DBSA complex particles according to Figure 3 were obtained, with PVC particles adhering to their surfaces.

#### Example 5

Three different blends were prepared in a friction mixer by using the mixing method according to Example 4. The PVC was PVC S88Y, the polyaniline complex was C1/2

EB87/90 A70 B30, and it had been ground fine in advance. In addition, DOP was added to 2 blends, and the DOP was mixed with the other components while the temperature was 60 °C.

Blends:

- 5 1. PVC 100 phr, DOP 15 phr, and complex 30 phr
2. PVC 100 phr, complex 30 phr
3. PVC 100 phr, DOP 20 phr, complex 30 phr

The results obtained were homogenous dry blends, which were further tested for electrical conductivity, outer appearance, and further processibility. The outer appearance was noted by visual observation to be good, further processibility proved to be excellent. Electrical conductivity was measured according to SFS standard 4372, and the conductivity level of all blends was within the range  $10^{-6}$  -  $10^{-8}$   $\Omega$ .

#### 15 Example 6

30 phr of polyaniline complex CI/9 EB96 A70B30, which had been milled in a disintegrator, 100 phr of PVC S88Y, and 10 phr of DOP were mixed as in Example 5. A microscopic picture, Figure 3, was taken of the dry blend. The figure shows that the obtained dry blend consists of PVC particles with polyaniline-DBSA complex particles adhering to their surfaces. The particles are of an even quality and the formed blend is homogenous.

#### Example 7

With the mixing proportions and mixing method according to Example 6, a dry blend was prepared on an industrial scale (an approx. 100 kg batch) by using a blend containing 30 phr of polyaniline complex, 100 phr of PVC, and 10 phr of DOP. The dry blend thus obtained was highly homogenous, it did not produce any dust, and the dry blend was easy to batch. PVC floor covering was made from the dry blend. The outer appearance of the floor covering was good and even. The electrical conductivity measured of the floor covering was in accordance with the standard. The electrical conductivities of floor coverings made from the dry blend were more even and better controllable than those of floor coverings made by conventional methods.

### Example 8

Two blends were prepared, each having the same ingredients as follows: 51 g of so-called floor covering mix (contains the PVC, stabilizers, etc.), 8 g of a polyaniline complex containing a Zn-DBSA plasticizer, 3 g of  $\text{TiO}_2$ , and 3 g of a color pigment.

- 5 The first blend was prepared using a known melt-mixing method, and the second blend was prepared using the dry-mixing method according to the invention. Electrical conductivities were measured from the obtained blends. The result was that the electrical conductivity of the blend obtained by the melt-mixing method was 5 M $\Omega$ , whereas that of the blend obtained by the dry-mixing method was, repeatedly measured, as high as
- 10 40 k $\Omega$ . The difference in electrical conductivity between the blend prepared by the melt-mixing method and the dry blend according to the invention is thus highly significant - the differences are up to several decades in favor of the dry blend according to the invention.
- 15 It can be noted on the basis of the above that the plastics dry blend according to the invention is, with respect to its technical properties, handlability, outer appearance, and processibility, a material highly practical and usable as a raw material for industry using conductive polymer materials.

## Claims

1. An electrically conductive dry blend material which contains a matrix polymer/matrix polymers and a conductive component, and the acidity of which is adjustable, characterized in that the electrically conductive component in the dry blend is a  
5 polyaniline complex doped with a protonic acid and plasticized with a plasticizer which melts at a temperature below 125 °C and, while in molten state, causes the electrically conductive polyaniline particles to adhere to the matrix polymer particles.
2. A dry blend material according to Claim 1, characterized in that the polyaniline  
10 complex doped with a protonic acid is plasticized with a plasticizer which melts at a temperature below 120 °C.
3. A dry blend material according to Claim 1 or 2, characterized in that in the dry blend the matrix polymer particles and the polyaniline complex particles are homo-  
15 genously mixed and that the homogeneity is retained during storage and transport of the blend.
4. A dry blend material according to Claim 1, 2, or 3, characterized in that the plasticizer is a compound formed by a protonic acid and a metal compound, preferably  
20 a Zn-DBSA compound formed by dodecylbenzenesulfonic acid and zinc oxide and melting at approx. 110 °C.
5. A dry blend material according to any of above Claims 1-4, characterized in that the molar ratio of the plasticizer to the doped polyaniline complex is within the range 1  
25 : 0.1 - 1 : 3, preferably within the range 1 : 0.25 - 1 : 1, and most preferably within the range 1 : 0.5 - 1 : 0.7.
6. A dry blend material according to any of above Claims 1-5, characterized in that the electrical conductivity of the dry blend is at a level  $> 10^9$  S/cm, preferably at a  
30 level  $> 10^6$  S/cm, and most preferably at a level  $> 10^3$  S/cm.
7. A dry blend material according to any of above Claims 1-6, characterized in that the acidity of the dry blend is within the pH range 3.5 - 7.

8. A dry blend material according to any of above Claims 1-7, **characterized** in that the dry blend may contain, in addition to the matrix polymer and the doped polyaniline complex, also softeners, fillers, and other additives required.
- 5 9. A dry blend according to any of above Claims 1-8, **characterized** in that the matrix polymers used may be any polymers commonly used in plastics blends, preferably homo- or copolymers based on olefins, styrene, vinyl polymers or acrylic polymers, mixtures thereof, or thermoplastic condensation polymers.
- 10 10. A dry blend according to Claim 9, **characterized** in that the matrix polymer used is polyolefins, preferably polyethylene or polypropylene, or polyvinyl chloride.
11. A dry blend according to any of above Claims 1-10, **characterized** in that the matrix polymer particles and the polyaniline complex particles may be, with respect to  
15 their particle sizes, a) of equal size, b) the matrix polymer particles larger than the complex particles, or c) the matrix polymer particles smaller than the complex particles.
12. A dry blend according to any of above Claims 1-11, **characterized** in that the  
20 proportion of the conductive polyaniline complex in the blend is within the range 1-50 % by weight, preferably within the range 1-25 % by weight, and most preferably within the range 3-15 % by weight.
13. A method for the preparation of an electrically conductive dry blend material  
25 which contains a matrix polymer/matrix polymers and a conductive component and the acidity of which is adjustable, **characterized** in that a polyaniline complex doped with a protonic acid and plasticized with a plasticizer which melts at a temperature below 125 °C is mixed with the matrix polymer in a dry-mixing apparatus the temperature of which is maintained at a temperature below 125 °C, most preferably below 120 °C,  
30 but above 80 °C.
14. A method according to Claim 13, **characterized** in that the polyaniline doped with a protonic acid is a polyaniline doped with sulfonic acid or its derivative, most



preferably a polyaniline doped with dodecylbenzenesulfonic acid.

15. A method according to Claim 13 or 14, **characterized** in that the polyaniline doped with a protonic acid is plasticized with a Zn-DBSA compound formed by dodecylbenzenesulfonic acid and zinc oxide, the compound melting at approx. 110 °C.
16. A method according to any of Claims 13-15, **characterized** in that the molar ratio of the plasticizer to the doped polyaniline is within the range 1 : 0.1 - 1 : 3, preferably within the range 1 : 0.25 - 1 : 1, and most preferably within the range 1 : 0.5 - 1 : 0.7.
17. A method according to any of above Claims 13-16, **characterized** in that, before the dry mixing of the doped polyaniline complex with the matrix polymer, the complex is milled to a particle size of 0.5 mm - 1.5 mm.
18. A method according to Claim 13, **characterized** in that the doped polyaniline complex which contains a plasticizer is mixed with the matrix polymer in a high-speed mixer, preferably a friction mixer, by raising the temperature to the melting point range of the plasticizer which melts at a temperature below 125 °C, preferably at a temperature below 120 °C, and most preferably at approx. 110 °C, and by continuing the mixing at this temperature for 10-30 min to produce a homogenous blend, and by cooling the blend while mixing is continued.
19. A method according to any of above Claims 13-18, **characterized** in that the dry blend is prepared in a master batch form, which is further dry mixed with additional matrix polymer.
20. A method according to any of above Claims 13-19, **characterized** in that softeners, fillers, and additives required may be added to the dry blend.
21. A method according to any of above Claims 13-20, **characterized** in that the matrix polymers used may be any polymers commonly used in plastics blends, preferably homo- or copolymers based on olefins, styrene, vinyl polymers or acrylic poly-

mers, or mixtures thereof, or thermoplastic condensation polymers, and preferably polyolefins, such as polyethylene or polypropylene, or polyvinyl chloride.

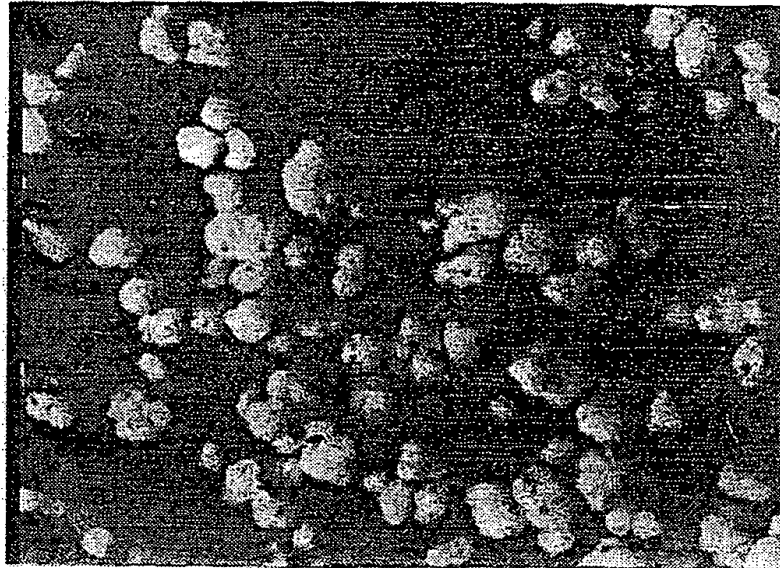


FIG 1



FIG 2

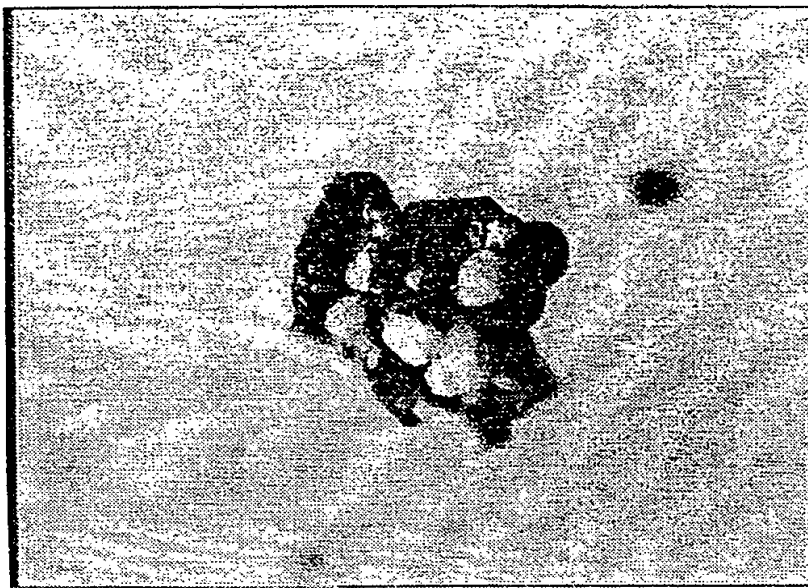


FIG 3



FIG 4

3/3

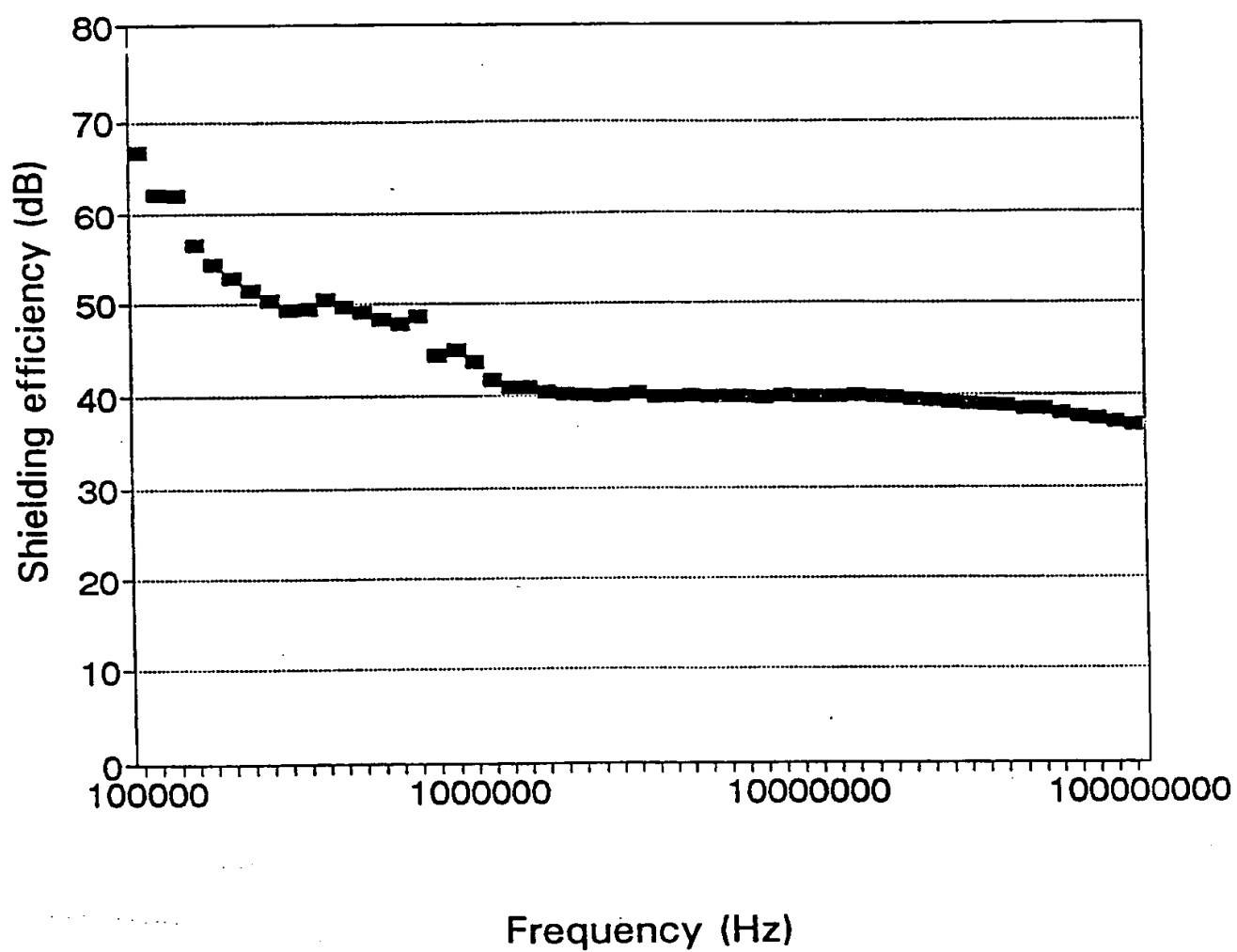


FIG 5

## INTERNATIONAL SEARCH REPORT

International application No.

T/FI 95/00085

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: H01B 1/12, C08L 79/02 // C08K 3/10, C08K 5/42

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: H01B, C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPIL, CA, CLAIMS

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0582919 A2 (NESTE OY), 16 February 1994 (16.02.94), page 8, line 39 - line 41, table 1  -- -----	1-22

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

## \* Special categories of cited documents:

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- "E" earlier document but published on or after the international filing date
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Date of the actual completion of the international search

18 July 1995

Date of mailing of the international search report

18-07-1995

Name and mailing address of the ISA/  
Swedish Patent Office  
Box 5055, S-102 42 STOCKHOLM  
Facsimile No. +46 8 666 02 86

Authorized officer

Hans Bäckström  
Telephone No. +46 8 782 25 00

Information patent family members

International application No.

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